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## TABLE OF CONTENTS

	Pages
Carbon Dioxide in the Atmosphere.....	1-8
Space Science Computation Assistance.....	9-10
OGO-6 Data Analysis Studies.....	10-13
Figure Captions.....	14
Figures.....	15-17

## Carbon Dioxide in the Atmosphere

F. S. Johnson

Although there is relatively little carbon dioxide in the atmosphere, there is evidence of great quantities having been removed from the atmosphere. A much greater quantity is present dissolved in sea water than is present in the atmosphere. However, even this amount is dwarfed by the carbon that has been deposited in carbonate rocks; these deposits contain carbon dioxide that has been withdrawn from the atmosphere in earlier geological times. The quantity of carbon dioxide required to provide the sedimentary carbonate is about  $2 \times 10^{23}$  g, or an average over the entire surface area of the earth of  $4 \times 10^4$  g cm<sup>-2</sup>, about one hundred thousand times the 0.45 g cm<sup>-2</sup> now present in the atmosphere and over a thousand times the 27 g cm<sup>-2</sup> present in the ocean.

The above numbers show that either there once was a much greater concentration of carbon dioxide in the earth's atmosphere or there has been a continuing source of carbon dioxide for the atmosphere that has been steadily transferred to carbonate deposits. The geologic evidence on this is clear that there was not a single early release into the atmosphere followed by its gradual removal by geologic processes. Rather, there has been a more or less continual supply over geologic time, and the source is identified as volcanic gases. This amounts to a continuous degassing of the earth's interior. With the recent concept of plate tectonics, it is possible to identify the volcanoes responsible for most of the release of new carbon dioxide from the earth's interior as those along the mid-ocean ridges. The most important gases that have been released in this manner, and

their amounts, are as follows:

H <sub>2</sub> O	3 x 10 <sup>5</sup> g cm <sup>-2</sup>
CO <sub>2</sub>	4 x 10 <sup>4</sup>
N <sub>2</sub>	10 <sup>3</sup>

Most of the water has condensed to form the oceans; most of the carbon dioxide has been converted into sedimentary carbonate deposits by processes to be described later; and most of the nitrogen has remained in the atmosphere because it is relatively inert chemically.

The earth's interior is incompletely oxidized, and no free oxygen is emitted by volcanoes. Oxygen in the atmosphere is a byproduct of two processes. The first is photodissociation of water vapor by ultraviolet sunlight followed by the escape to space from the upper atmosphere of the hydrogen that is released by photodissociation. If the hydrogen did not escape but instead remained in the atmosphere, it would eventually become oxidized back to water vapor, and no net oxygen production would result. The second process is photosynthesis, in which water and carbon dioxide and energy from sunlight produce organic material, releasing oxygen in the process. In a manner similar to hydrogen, the organic material may eventually recombine with oxygen (by decay or combustion) to reform carbon dioxide and water, thus providing no net production of oxygen. Unlike hydrogen, the organic material cannot escape from the earth. However, it can sometimes end up protected from oxidation in sedimentary deposits, for example, in the form of coal. In this way a lasting contribution to the earth's oxygen supply can be produced by photosynthesis. Photosynthesis and the subsequent fossilization or deposition of organic material in

unoxidized form has provided most of the earth's supply of oxygen. Photodissociation of water vapor and the subsequent escape of hydrogen to space has also been important, but it represents a considerably smaller source.

It is estimated that  $3 \times 10^{16}$  g carbon per year is transferred from atmospheric carbon dioxide to organic material by photosynthesis. This occurs about half on land and half in the ocean, the latter mainly in the form of phytoplankton. A significantly larger amount of photosynthesis was once assumed to occur at sea before the very low level of productivity in temperate latitude mid-ocean areas was recognized. The annual consumption of carbon dioxide in photosynthesis is about  $1.1 \times 10^{17}$  g, which may be compared with the total carbon dioxide content of the atmosphere of about  $2.3 \times 10^{18}$  g. Clearly, were it not for other important processes, the carbon dioxide content of the atmosphere would be greatly reduced within a few decades by photosynthesis. The first important process to take into account is the decay and oxidation of organic material; if this were complete, as much carbon dioxide would be returned to the atmosphere as is taken from it by photosynthesis. Actually, decay of organic material is about 99.9% complete, only about 0.1% escaping decay by deposition is unoxidized form in sedimentary deposits. This lengthens the time that would be required to use up the atmospheric carbon dioxide to tens of thousand of years. Since the reservoir of carbon dioxide in the ocean is accessible to the atmosphere, the time is further extended to something like a million years - still a short time on a geologic scale, emphasizing the importance of a continuing supply from the earth's interior and the

release of carbon dioxide by weathering of sedimentary deposits containing organic or fossilized carbon.

Weathering is a continual process on earth - weathering of both igneous rocks that in many cases consist of fresh materials from the earth's interior and also sedimentary rocks that represent the end product of previous weathering processes.

The presence of carbon dioxide in the air causes rain to be slightly acidic, and this greatly accelerates the weathering of rocks and the transport of dissolved materials to the sea. The pH of rainwater is about 6 (otherwise pure water saturated with air, including carbon dioxide at its partial pressure in the atmosphere, has a pH near 5.2). When rainwater comes into contact with minerals at the earth's surface, especially calcium, the pH rises, and values near 7 are commonly encountered in river water. The rivers carry a continual load of dissolved minerals to the sea, where they in part accumulate and in part become transferred into geologic deposits, either by direct precipitation, the slow growth of deposits from solution at the ocean bottom, or by accumulation of the remnants of plant and animal life.

The weathering of rocks also places an important demand on the earth's oxygen supply. Igneous rocks are less than fully oxidized, and as they weather away, exposing new material, much oxidation takes place. Examination of the oxidation produced in such weathering makes it clear that the amount of oxygen that has been removed from the atmosphere is at least 15 times greater than the amount of oxygen now found in the atmosphere. Most of the oxygen that has been removed from the atmosphere

is at least 15 times greater than the amount of oxygen now found in the atmosphere. Most of the oxygen that has been removed from the atmosphere by oxidation of mineral materials (including volcanic gases) is now associated with minerals in sedimentary rocks, which on average are more highly oxidized than the igneous rocks whose weathering provided their basic materials.

There are two important forms in which carbon occurs in sedimentary rocks - unoxidized organic material and carbonate. The normal fate of organic material is decay and oxidation, but there are a few situations where this fate may be escaped. Peat bogs provide one obvious example, and with passage of time these may be converted to coal. There are also some limited ocean basins in which circulation is restricted and where anoxic (oxygen free) bottom conditions develop. With the oxygen-free bottom conditions, organic materials that fall from growth regions near the surface escape oxidation; these may end up as oil shales or as oil deposits. However, the greatest portion of the unoxidized organic material deposited in sediments is in highly dispersed forms, often in shales, but in forms not suitable for exploitation as fuel. The total amount of carbon in the form of oil and coal is estimated to be about  $3 \times 10^{18}$  g, while unoxidized organic material in more dispersed form is thought to contain  $10^{22}$  g carbon.

The other geologic sink for carbon is carbonate rocks. The amount of carbon in these is estimated to be  $4 \times 10^{22}$  g. These are formed in two ways, direct chemical deposition and through life processes. Calcium and magnesium, especially calcium, are the principal elements associated with carbonates.

The weathering of calcium from igneous rocks is greatly enhanced by the presence of carbon dioxide in water. Even more calcium is weathered from exposed old sedimentary rocks, as the solubility of calcium carbonate is highly sensitive to the presence of carbon dioxide. The rate at which calcium is transported to sea in rivers would supply the calcium content of the oceans in less than  $10^6$  years, or all the calcium in sedimentary rocks in about  $3 \times 10^8$  years, less than one tenth of the time that rivers have flowed into oceans on earth. This indicates that most calcium in river water is recycled, coming mainly from weathering of old sedimentary rocks, with only about 6% being new calcium coming from weathering of igneous rocks.

The removal of carbonate and calcium from sea water is partly physico-chemical and partly biological. In warm areas of the ocean, carbon dioxide is driven out of solution and calcium carbonate is precipitated, eventually to appear in the form of calcite. The other means is by biological processes - deposition of shells or other animal parts.

The relatively rapid (on a geologic time scale) recycling of sedimentary rocks also exposes unoxidized organic materials. These materials then become oxidized, making a large demand on the earth's new oxygen production. Of each  $10^6$  g of oxygen produced in photosynthesis, all but about  $10^3$  g is used in the oxidation of the recently formed organic materials. Of the  $10^3$  g remaining, about 900 are required for oxidation of the old unoxidized organic material from newly weathered sedimentary rocks. This leaves about 100 g available to the atmosphere, but 90 g



of this is needed to oxidize newly weathered igneous rocks, leaving only about 10g as the lasting contribution to the atmosphere. The permanent release to the atmosphere of such a small fraction of the oxygen production from photosynthesis is inadequate to explain the development of the oxygen content of the atmosphere in a reasonable time period; this reflects the fact that net oxygen contributions to the atmosphere were much greater before the negative feedback provided by exposure of unoxidized organic materials in sedimentary rocks by weathering became effective.

The pathways for movement of carbon and oxygen through the atmosphere are shown in simplified form in Figure 1. Both have come principally from the earth's interior through volcanoes in the form of carbon dioxide and water vapor. The numbers beside some of the arrows on Figure 1 indicate the amount of carbon in g/yr involved in the process and the numbers in some of the boxes indicate the grams of carbon in that reservoir. Both on land and in the oceans (and other water bodies) photosynthesis consumes carbon dioxide and releases oxygen to the atmosphere. The organic material produced by photosynthesis mainly undergoes decay and oxidation, consuming oxygen and releasing carbon dioxide. However, a small fraction ( $\sim 0.1\%$ ) escapes oxidation and becomes fossil carbon, only a small fraction of which ( $\sim 0.03\%$ ) is in forms suitable for use as fuel. The weathering of sedimentary rocks, of course, exposes some of the fossil carbon, which then becomes oxidized and returns carbon dioxide to the atmosphere. This process provides a natural control on oxygen in the earth's atmosphere, consuming most of the new oxygen deposited in the

atmosphere by the excess of photosynthesis over decay of organic material. It is now completely overwhelmed (by a factor of about a hundred) by the burning of fossil fuel. Thus the oxygen content of the atmosphere must now be decreasing, even though by only an inconsequential amount.

The increase in atmospheric carbon dioxide as a result of burning fossil fuels has been well documented. The increase since the beginning of the century has been about 6%, from about 300 to 320 ppm, and the rate of increase is now near 0.8 ppm per year. The annual increase is only about one third of the amount released in fossil fuel combustion, the remaining two-thirds being taken up by the oceans where it produces an inconsequential increase in that much larger reservoir. The exchange time between the atmosphere and the ocean is about five years.

Although carbon dioxide in the atmosphere (along with water vapor and ozone) is important in providing a greenhouse effect that elevates the temperature of the earth's surface well above the average value that would exist without an atmosphere, the increased warmth due to increased carbon dioxide from combustion of fossil fuel is small. The possibility that the increased warmth might cause carbon dioxide to be driven out of solution from the oceans and greatly accelerate the warming trend has been investigated and found to be very unlikely.

A large fraction of the carbon dioxide in the ocean is contained in cold bottom waters. It is formed by the decomposition and oxidation of organic material falling from the upper levels of the ocean. That is, the carbon involved is carried into the bottom waters in a form different

than carbon dioxide, and the flow of carbon dioxide in the ocean is from the cold bottom water to the surface levels, associated with the slow circulation of the ocean. This is brought about mainly by the sinking of surface water at high latitudes in water.

Space Science Computation Assistance

J. E. Midgley

The PDP 11-45 computer procured 18 months ago primarily to handle space-related data processing has proven very useful and cost effective during the past year and promises to be even more so during the coming year. It was used by Dr. Donald Sterling to develop and debug the software that is currently being used by Dr. W. B. Hanson on the Atmospheric Explorer Sigma 7 system at Goddard Space Flight Center to analyze their RPA data. The hardware calibration of the RPA's was done using an Analog to Digital link to the 11-45, which stores the data on tape for later analysis. It has been used for analysis of Dr. W. J. Heikkila's ISIS data, although most of his programs are still in the process of conversion and the heavy load from that source will not begin for a few months. Dr. B. A. Tinsley and a student have used it for calculation of ionization redistribution in the F region due to wind effects, but memory limitations have made it more efficient to do that problem elsewhere; the output of that program, however, is used on the 11-45 to calculate air-glow intensities, and his ground based-air-glow data are analyzed on the 11-45. A seven track tape unit was installed at mid-year and since then Dr. F. R. Allum has used the computer a great deal to process magnetic field data from

Explorer 34 to be used in conjunction with cosmic ray anisotropy data from the same satellite. Dr. J. P. McClure is using the computer to process and display data on the ionospheric F region irregularities obtained at the Jicamarca Radar Observatory.

Many investigators are using the facility for theoretical calculations. Dr. R. A. Heelis and Mr. R. W. Spiro are investigating polar ionospheric escape under quite different conditions. Dr. S. Sanatani is calculating theoretical ionograms and Mr. Shiv Kumar is studying equatorial ionospheric currents. Dr. E. L. Breig has done numerical calculations on longitudinal and seasonal variations in ion composition and temperature in conjunction with ISIS-II and OGO-6 measurements, and on transport processes associated with heavy ions introduced as an artificial perturbation in the ionosphere.

The only real limitation of the system is memory size and a big step toward alleviating that was taken this year with the addition of 192K bytes of core. Unfortunately the current DEC software cannot support programs larger than about 50K bytes and the extra storage is now useful only for temporary data storage--a "fast disc" in effect. Work is now under way to change this situation. The work load has been steadily increasing all year as more projects get their programs converted from other facilities, and the computer now runs continuously for a full shift five days a week. This month we expect to add another half shift.

#### OGO-6 Data Analysis Studies

E. L. Breig

The retarding potential analyzer on board the OGO-6 satellite has

provided comprehensive global measurements of the nighttime ion temperature in the altitude region between 400 and 1100 km. These data provide the basis for theoretical investigations and analyses relative to the altitude dependence of the nighttime ion temperature, and to its variation with latitude, longitude and season.

In addition to its role as an ionizing agent, the absorption of solar euv radiation provides an important thermal energy source for the thermosphere. A complex chain of energy transfer processes establishes a condition of thermodynamic non-equilibrium among the various atomic and molecular species, the ions being heated by the ionospheric electron gas and losing energy to the neutrals. Hence an understanding of the several variabilities of the F-region ion temperature can provide information on the thermal budget available for neutral heating, and also provide clarification of the relevant physical mechanisms involved in the various modes of energy transfer. The in-situ OGO-6 satellite measurements of ion temperature provide data on the magnitudes and variabilities of the temperature of the atmospheric ions, major unknowns in our knowledge and understanding of the upper atmosphere. Data analysis and interpretation should yield information on those physical processes related to the input, storage, transport, and loss of thermal energy in the thermosphere.

Theoretical studies are in progress concerning the altitude variations of the F-region ion temperature for the basic time period between late December, 1969, and early February, 1970. Motion of the OGO-6 satellite orbit during this period was such as to provide good nighttime coverage of the 400-900 km altitude range throughout low and mid latitudes in the winter hemisphere. Although the studies are to ultimately include

other aspects of the ion temperature problem, the current emphasis is on data analysis and interpretation of the altitude dependence of such ion temperatures at selected dip latitudes, and how such altitude profiles vary with longitude.

Relevant satellite data for the above time period have been summarized in a form conducive for theoretical analysis, providing sets of data relating altitude and ion temperature,  $T_i$ . These data sets are further classified according to geomagnetic dip latitude, and cover the region from 0 to 55 degrees in the winter hemisphere. The initial stages of analysis have focused primarily on those regions near 30 and 50 degrees dip latitude.

Contrary to preliminary indications, the data have demonstrated a significant dependence of the  $T_i$  altitude profile on longitude. For a given altitude and dip latitude, the ion temperature is found to maximize in the geographic longitude region between  $0^\circ$  and  $90^\circ\text{W}$ , with its lowest values generally between  $50^\circ\text{E}$  and  $150^\circ\text{E}$ . This general longitudinal behavior is observed above 600 km at both 50 and 30 degrees dip latitude, and is discernible to below 500 km at 50 degrees latitude.

The net consequence of this longitudinal effect is that meaningful comparisons of altitude profiles of  $T_i$  require a careful concurrent consideration of longitude. Figure 2 illustrates the altitude and longitude dependences of  $T_i$  at  $50^\circ$  dip latitude, and compares altitude profiles between those longitude regions of maximum and minimum ion temperatures. A special feature of these profiles is the steady rapid rise in  $T_i$  above 500 km in those longitude regions with the highest temperature; by comparison,  $T_i$  in the low temperature longitude region remains relatively low to near 700 km before increasing with a very sharp

gradient over the next few hundred kilometers.

The altitude effects at  $30^\circ$  dip latitude are distinctly different from those described near  $50^\circ$ . At  $30^\circ$  there is no noticeable longitude variation in  $T_1$  below 600 km; however, there is a distinct ion temperature maximum in the altitude profile near 450 km, followed by a temperature minimum between 500 and 600 km. These general characteristics are illustrated in Figure 3. Although similar features have been indicated in the corresponding  $50^\circ$  profile of Figure 2, such a temperature peak is not as well defined in the data as that appearing at  $30^\circ$  dip latitude. Above 600 km, a longitudinal effect must also be considered; the profiles shown are strictly applicable only for the longitude region of low ion temperature. Although  $T_1$  in the high temperature region approaches  $2000^\circ$  or greater near 700 km, the data are too erratic in behavior to define a consistent altitude profile.

Work is in progress to isolate the underlying source for the maximum observed in the nighttime ion temperature data at  $30^\circ$  dip latitude, and to better define the longitudinal dependence of  $T_1$ . The present type of analysis is also being extended to other latitude regions.

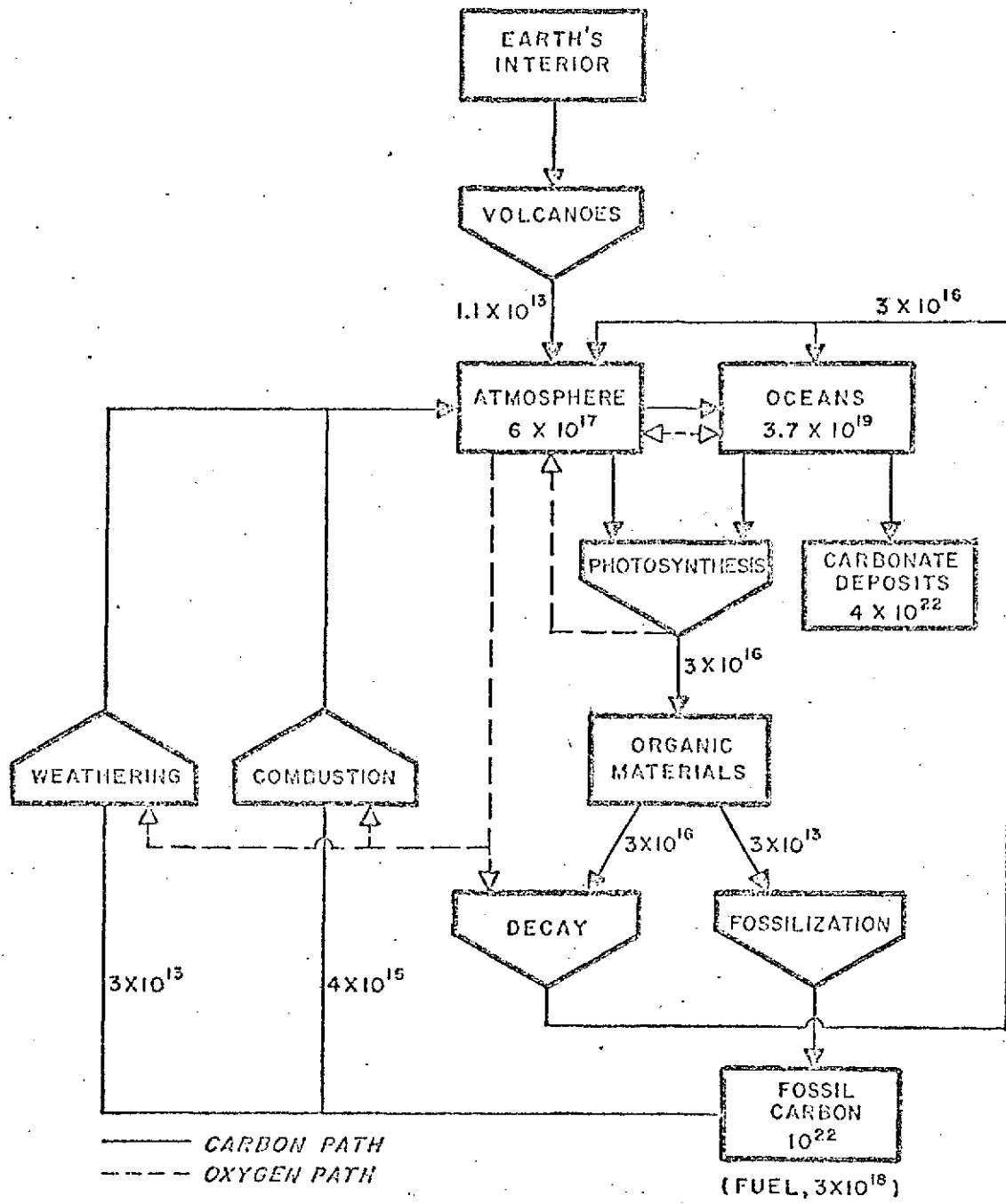
FIGURE CAPTIONS

Figure 1. Pathways of Carbon and Oxygen through the Earth's Atmosphere.

Figure 2. Variations of Nighttime Ion Temperature with Altitude and Longitude at  $50^\circ$  Magnetic Dip Latitude.

Figure 3. Altitude Variation of Nighttime Ion Temperature at  $30^\circ$  Magnetic Dip Latitude in the Low-Temperature Longitude Region.





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FIGURE 1

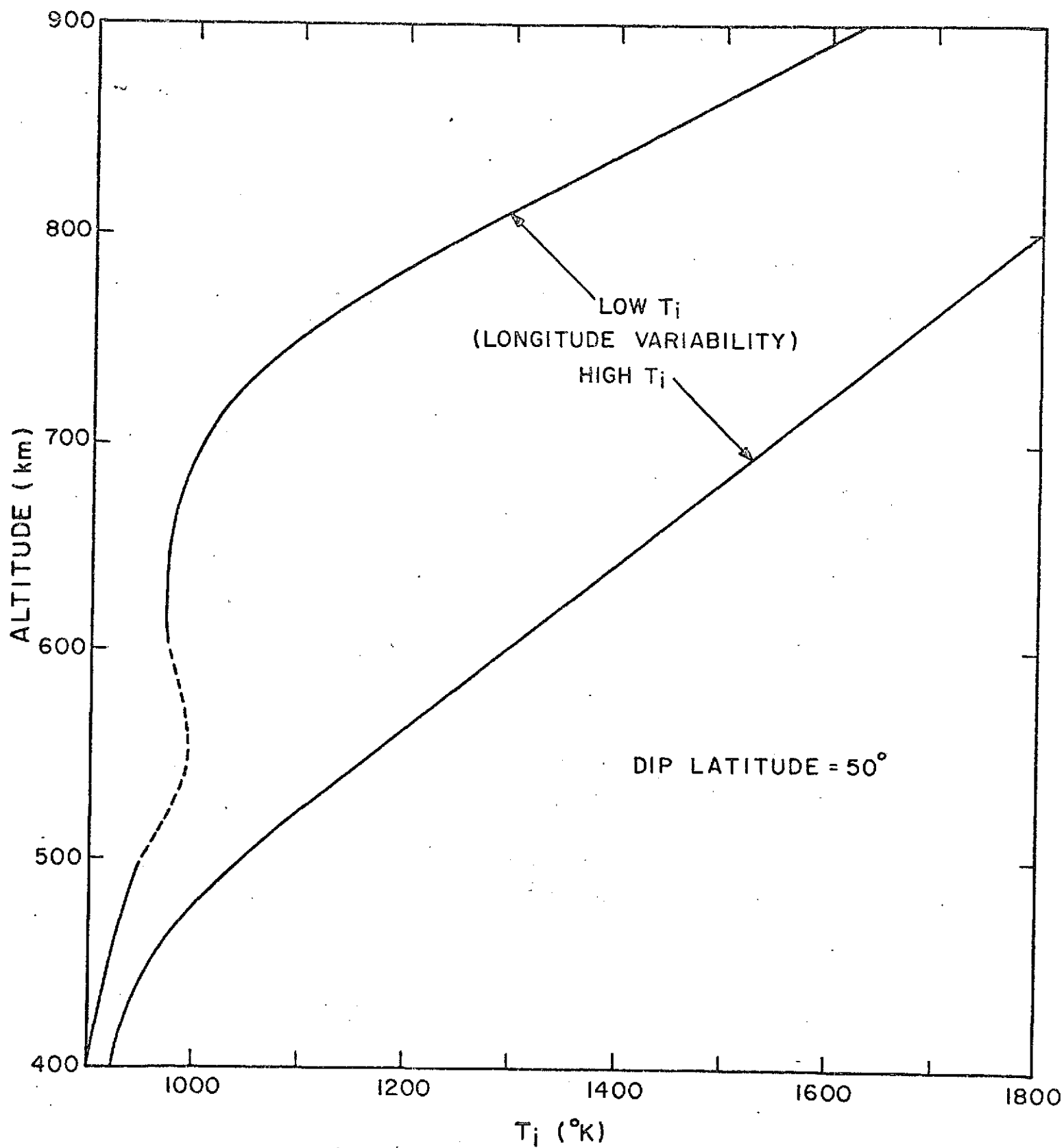


FIGURE 2

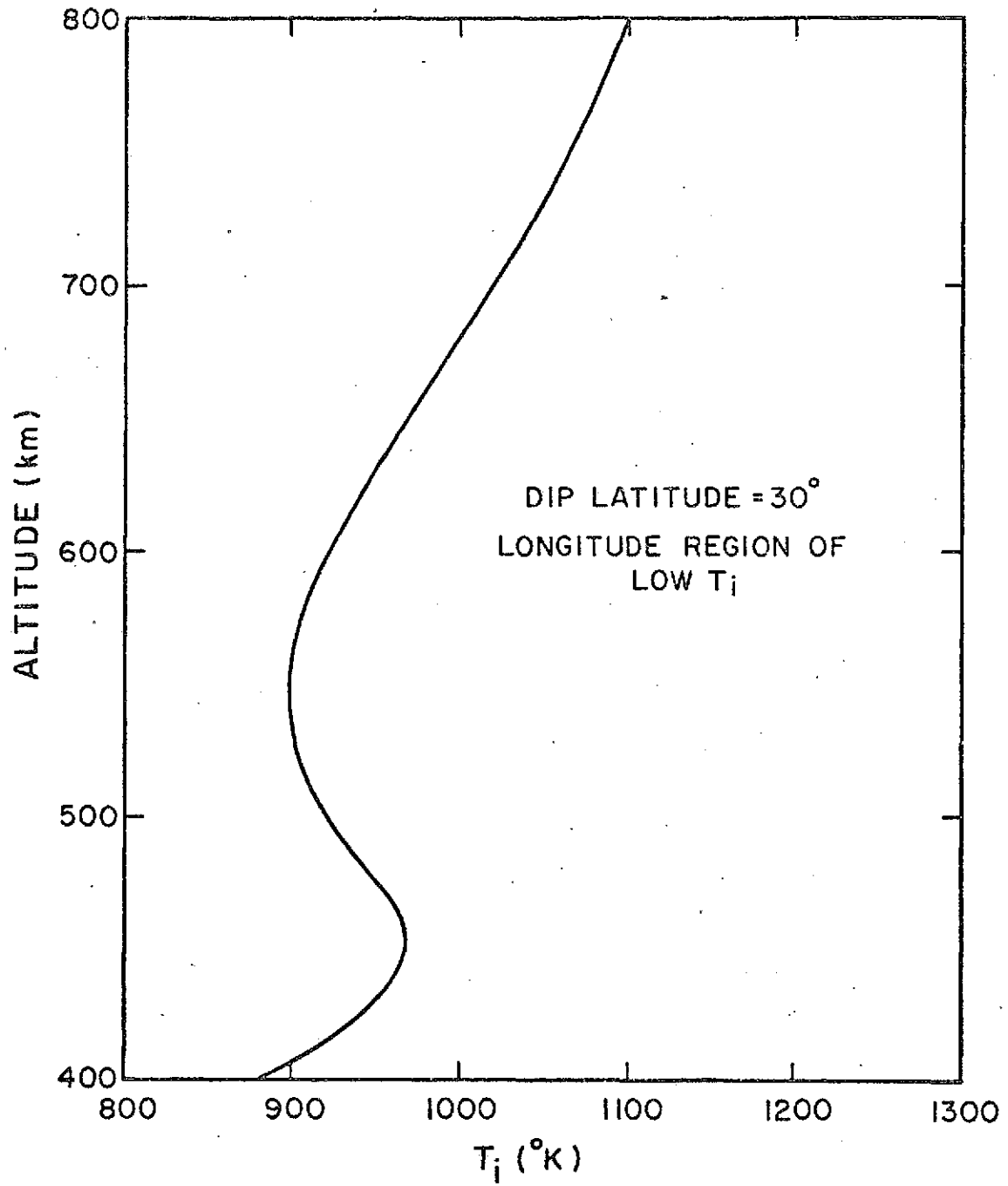


FIGURE 3